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IMPROVED COATED PESTICIDAL MATRICES,
A PROCESS FOR THEIR PREPARATION
AND COMPOSITIONS CONTAINING THEM

BACKGROUND OF THE INVENTION

Ins A1
Certain pesticidal agents are inactivated by ultra-
violet radiation from the sun. Because those pesticidal
agents are useful for the control of pests and are
5 applied in areas where they will be exposed to
ultraviolet radiation, there is a need for photostable
compositions containing those agents.

To prevent ultraviolet inactivation of pesticidal
agents, compositions have been prepared which contain
10 ultraviolet absorbers and/or reflectors and a pesticidal
agent.

U.S. Patent 3,541,203 describes a protected virus
composition for insect control. The preferred
composition includes a virus, an actinic light absorbing
15 material and a polymeric binder material. However, the
process used to prepare the preferred compositions of
U.S. Patent 3,541,203 requires the use of toxic materials
and numerous washing steps with flammable solvents thus
making it unsuitable for commercial manufacture.

20 U.S. Patent 4,948,586 discloses a microencapsulated
insecticidal pathogen. Four microencapsulated
compositions are shown to decrease the photoinactivation
of *Autographa californica* NPV. However, the microencap-

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sulated compositions retain only from 30.7 to 71.43% of the original activity upon exposure to sunlight. U.S. Patent 4,948,586 discloses a method of preparing microencapsulated insecticidal pathogens which has numerous steps and is both time-consuming and laborious. It is apparent that neither the process, nor the microencapsulated insecticidal pathogens, described in U.S. Patent 4,948,586, are entirely satisfactory for providing a product stable to ultraviolet radiation.

U.S. Patent 5,560,909 discloses a process for the preparation of insecticidal compositions which requires the modification of the charge of a charged polymer to precipitate the polymer and entrap the insecticide. However, this process is not entirely satisfactory because a small amount of the functional groups on the polymer will remain charged in the final product, resulting in a less efficacious product.

EP 697170-A1 discloses a process for the preparation of coated pesticidal agents which requires that the coating polymer be completely dissolved and which adjusts the pH of the coating solution to attain such dissolution. Unfortunately, such dissolution reduces some of the desirable properties of the coating polymer, resulting in a less efficacious product.

SUMMARY OF THE INVENTION

The present invention comprises an improved process for the preparation of a coated pesticidal matrix, which process comprises: a) preparing an aqueous mixture comprising a pesticidal agent, a pH-dependent polymer and water, wherein the pH is below the solubilization pH of the polymer; and b) drying the aqueous mixture to produce the coated pesticidal matrix. The aqueous mixture optionally includes a plasticizer, an ultraviolet protector, an activity enhancer and/or a glidant thus

resulting in their presence in the coated pesticidal matrix. Preferably, the pesticidal agent is a particulate chemical insecticide or a viral, bacterial or fungal insecticidal pathogen.

5 The present invention also comprises wettable powder pesticidal compositions which comprise coated pesticidal matrices, together with suitable carriers.

10 The present invention further comprises a method for improving the residual control of a pest comprising the application of a matrix made by the process of this invention.

15 It is an object of the present invention to provide a coated pesticidal matrix which retains the desirable properties of the coating polymer and thus retains a significant amount of its original pesticidal activity after exposure to ultra-violet radiation.

20 It is also an object of the present invention to provide an improved process for the preparation of a coated pesticidal matrix under mild conditions which avoid degradation of the pesticidal agent.

Other objects of this invention will be apparent to those skilled in the art from the following description and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

25 The improved process of this invention comprises:

30 a) preparing an aqueous mixture comprising a pesticidal agent, a pH-dependent polymer, optionally a plasticizer, optionally an ultraviolet protector, optionally an activity enhancer, optionally a glidant, and water, provided that the pH of the aqueous mixture is below the solubilization pH of the pH-dependent polymer; and

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b) drying the aqueous mixture of step (a) to produce a coated pesticidal matrix.

Advantageously, it has been found that coated pesticidal matrices, prepared from a pH-dependent polymer without converting a substantial number of free carboxylic acid groups in the polymer to their salt form, retain a high percentage of their original activity after exposure to ultraviolet radiation and have greater residual activity compared to coated pesticidal agents prepared by the coating process described in EP 697170-A1. The instant process accomplishes this by providing an aqueous mixture wherein the pH is below the solubilization pH of the pH-dependent polymer.

In a preferred embodiment of the present invention, coated pesticidal matrices prepared by the process of this invention comprise about 1 to 50% by weight of a pesticidal agent, about 5 to 50% by weight of a pH-dependent polymer, 0 to about 25% by weight of a plasticizer, 0 to about 30% by weight of an ultraviolet protector, 0 to about 75% by weight of an activity enhancer, and 0 to about 15% by weight of a glidant.

More preferred coated pesticidal matrices prepared by the process of this invention are those comprising about 5 to 35% by weight of a pesticidal agent, about 10 to 45% by weight of a pH-dependent polymer, 0 to about 25% by weight of a plasticizer, 0 to about 20% by weight of an ultraviolet protector, 0 to about 45% by weight of an activity enhancer, and 0 to about 10% by weight of a glidant.

The aqueous mixture of this invention may be dried using any conventional drying technique which allows the pH-dependent polymer to form a coating film on the outside, and a binding film inside, of the matrix particles. Preferably, the aqueous mixture is spray dried or air dried. The coated pesticidal matrices of

the present invention preferably have a particle size less than about 20 μm , and, more preferably, have a particle size of about 2 μm to 10 μm .

Pesticidal agents suitable for use in the present invention include chemical and biological insecticides, acaricides, nematocides, fungicides, herbicides, and the like, and mixtures thereof. In particular, pesticidal agents which are subject to inactivation of their desired activity by ultraviolet radiation are preferred pesticidal agents for use in this invention.

Chemical insecticides include, but are not limited to, arylpyrroles such as chlorfenapyr; amidinohydrazones such as hydramethylnon; hydrazinecarboxyamides such as those described in U.S. 5,543,573; 1,4-diaryl-2-fluoro-2-butenes such as those described in EP 811593-A1, including 1-[1-(*p*-chlorophenyl)-2-fluoro-4-(4-fluoro-3-phenoxyphenyl)-2-butenyl]cyclopropane, (R,S)-(Z)-; 1-substituted-2-(nitromethylene)imidazolidines such as imidacloprid and 1-(6-chloro-3-pyridyl)-2-(nitromethylene)imidazolidine; phenylpyrazoles such as fipronil; and the like, and mixtures thereof. The chemical insecticides of this invention, when in solid form, preferably have a particle size prior to coating of less than about 10 μm and, more preferably, have a particle size of about 0.1 μm to 5 μm .

Biological insecticides include all naturally occurring and genetically modified varieties of insect biological control agents such as viral pathogens, bacterial pathogens, and fungal pathogens. Viral pathogens suitable for use include DNA viruses, RNA viruses and unclassified insect viruses such as gonad-specific virus (GSV).

The DNA viruses include double stranded enveloped DNA viruses such as (Subfamily, then species)

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Entomopoxvirinae (*Melolontha melolontha* entomopoxvirus),
and *Eubaculovirinae* (*Autographa californica* MNPV;
Heliocoverpa zea NPV; *Trichoplusia ni* GV), as well as
double stranded nonenveloped DNA viruses such as
5 *Iridoviridae* (*Chilo* iridescent virus) and single stranded
nonenveloped DNA viruses such as *Parvoviridae* (*Galleria*
densovirus).

The RNA viruses include double stranded enveloped
RNA viruses such as *Togaviridae* (*Sindbis* virus),
10 *Bunyaviridae* (Beet leafcurl virus) and *Flaviviridae*
(*Wesselbron* virus), as well as double stranded
nonenveloped RNA viruses such as *Reoviridae* (*Corriparta*
virus) and *Birnaviridae* (*Drosophila* X virus), as well as
single stranded nonenveloped RNA viruses such as
15 *Picornaviridae* (*Cricket* paralysis virus), *Tetraviridae*
(*Heliothis armigera* stunt virus) and *Nodaviridae* (Black
beetle virus).

The Subfamily of double stranded DNA viruses
Eubaculovirinae includes two genera, nuclear polyhedrosis
20 viruses (NPVs) and granulosis viruses (GVs), which are
particularly useful for biological control because they
produce occlusion bodies in their life cycle. Examples
of NPVs include *Lymantria dispar* NPV (gypsy moth NPV);
Autographa californica NPVs such as V8vEGTDEL, V8vEGTDEL-
25 AaIT, AcMNPV E2, AcMNPV L1, AcMNPV V8, and AcMNPV Px1;
Anagrapha falcifera NPV (celery looper NPV); *Spodoptera*
littoralis NPV; *Spodoptera frugiperda* NPV; *Heliothis*
armigera NPV; *Mamestra brassicae* NPV; *Choristoneura*
fumiferana NPV; *Trichoplusia ni* NPV; *Heliocoverpa zea*
30 NPV; and *Rachiplusia ou* NPV; and the like. Examples of
GVs include *Cydia pomonella* GV (coddling moth GV), *Pieris*

brassicae GV, *Trichoplusia ni* GV, *Artogeia rapae* GV, *Plodia interpunctella* GV (Indian meal moth), and the like. Examples of entomopox viruses (EPVs) include *Melolontha melolontha* EPV, *Amsacta moorei* EPV, *Locusta*
5 *migratoria* EPV, *Melanoplus sanguinipes* EPV, *Schistocerca gregaria* EPV, *Aedes aegypti* EPV, *Chironomus luridus* EPV, and the like.

Bacterial pathogens suitable for use include, but are not limited to, *Bacillus thuringiensis*, *Bacillus*
10 *lentimorbus*, *Bacillus cereus*, *Bacillus popilliae*, *Photobacterium luminescens*, *Xenorhabdus nematophilus*, and the like. Fungal pathogens suitable for use include, but are not limited to, *Beauveria bassiana*, *Entomophthora* spp., *Metarrhizium anisopliae*, and the like.

15 AcMNPV E2 is described in EP 621337, and co-pending U.S. Serial No. 08/009,264, filed January 25, 1993, which is incorporated herein by reference. AcMNPV V8 and V8vEGTDEL are described in U.S. Patent 5,662,897 which is incorporated herein by reference. V8vEGTDEL-AaIT is
20 described in EP 697170-A1 and co-pending U.S. Serial No. 08/322,679, filed July 27, 1994. AcMNPV Px1 is described in co-pending provisional U.S. Serial No. 60/084,705, filed May 8, 1998, which is incorporated herein by reference.

25 Herbicides suitable for use in the present invention include chemical and biological herbicides. Chemical herbicides include, but are not limited to, dinitro-anilines such as pendimethalin and trifluralin; imidazolinones such as imazethapyr, imazaquin,
30 imazamethabenz-methyl, imazapyr, imazamox and imazapic; haloacetanilides such as alachlor, metolachlor, and propachlor; and the like; and mixtures thereof. Biological herbicides include, but are not limited to,

fungus pathogens such as a *Dactylaria higginsii*, and the like, and mixtures thereof.

pH-Dependent polymers suitable for use in the present invention include polymers which are essentially insoluble below about pH 5.5, such as ethyl acrylate/methacrylic acid copolymers, methyl methacrylate/methacrylic acid copolymers, methacrylic acid/methyl acrylate/methyl methacrylate copolymers and the like, and mixtures thereof. Preferred pH-dependent polymers include ethyl acrylate/methacrylic acid copolymers wherein the ratio of free carboxyl groups to esters is about 1:1 (Eudragit® L 30 D, solubilization pH > 5.5, available from Röhm Pharma GmbH, Weiterstadt, Germany; and Kollicoat® MAE 30 D, solubilization pH > 5.5, available from BASF, Ludwigshafen, Germany), methyl methacrylate/methacrylic acid copolymers wherein the ratio of free carboxyl groups to esters is from about 1:1 to about 1:2 (Eudragit® S100, 1:2 ratio, solubilization pH > 7.0, available from Röhm Pharma; and Eudragit® L100, 1:1 ratio, solubilization pH > 6.0, available from Röhm Pharma), methacrylic acid/methyl acrylate/methyl methacrylate copolymers wherein the ratio of methacrylic acid, methyl acrylate and methyl methacrylate monomers is about 1:5:2 to 3:7:3 (Preparation 4110D, 1:6.5:2.5 ratio, solubilization pH > 7.2, available from Röhm Pharma), and mixtures thereof.

The pH-dependent polymer should be essentially insoluble below about pH 5.5 to prevent premature release of the pesticide when the coated pesticidal matrix is applied to the locus of a pest. In addition, when the pesticidal agent is an insecticide, the pH-dependent polymer should be soluble in the environment of the insect's gut so that the pesticidal agent may be readily released from the coated pesticidal matrix. Preferably, the pH-dependent polymer should be soluble above about pH

In a preferred embodiment of the process of this invention, the methyl methacrylate/methacrylic acid copolymer is partially solubilized with base to reduce agglomeration of the copolymer particles prior to drying. However, it should be understood that the amount of base added is well below the amount required to fully solubilize the copolymer. Typically, less than about 10% of the free carboxylic acid groups of the copolymer are converted to salts. Bases suitable for use to partially solubilize the methyl methacrylate/methacrylic acid copolymers of this invention include ammonium hydroxide, alkali metal hydroxides, alkaline earth metal hydroxides and the like, with ammonium hydroxide being preferred.

Ultraviolet protectors are used in the present invention to reduce the photoinactivation of the pesticidal agent. Ultraviolet protectors suitable for use include ultraviolet absorbers and ultraviolet reflectors or mixtures thereof. Ultraviolet absorbers include various forms of carbon, such as carbon black (charcoal); benzophenones, such as 2-hydroxy-4-methoxybenzophenone (CYASORB® UV9, available from Cytec

Industries, West Paterson, New Jersey), 2,2'-dihydroxy-4-methoxybenzophenone (CYASORB® UV24, available from Cytec Industries), 2-hydroxy-4-acryloyloxyethoxybenzophenone (CYASORB® UV2098, available from Cytec Industries),

5 2-hydroxy-4-n-octoxybenzophenone (CYASORB® UV531, available from Cytec Industries); dyes, such as congo red, malachite green, malachite green hydrochloride, methyl orange, methyl green, brilliant green, acridine yellow, FDC green, FDC yellow, FDC red, and the like.

10 Ultraviolet reflectors include titanium dioxide and the like. Preferred ultraviolet protectors include carbon black, benzophenones, dyes and titanium dioxide; with titanium dioxide, carbon black, CYASORB® UV9 and CYASORB® UV24 being most preferred.

15 Activity enhancers are used in this invention to enhance pesticidal activity of the pesticidal agent. Activity enhancers suitable for use in this invention include fluorescent brighteners described in U.S. Patent 5,124,149 and stilbene compounds described in U.S. Patent

20 5,246,936, both incorporated herein by reference. In addition to enhancing pesticidal activity, the stilbene compounds also provide some protection from ultraviolet radiation. Preferred stilbene compounds are the analogues of 4,4'-diamino-2,2'-stilbene disulfonic acid,

25 namely, a Calcofluor White (available from Sigma Chemical Co., St. Louis, Missouri) such as Calcofluor White M2R, Calcofluor White ABT, Calcofluor White LD, Calcofluor White RWP, etc.; a Blancophor (available from Mobay Chemicals, Pittsburgh, Pennsylvania) such as Blancophor

30 BBH, Blancophor MBBH, Blancophor BHC, etc.; an INTRAWITE® (a heterocyclic stilbene derivative, available from Crompton and Knowles Corp., Charlotte, North Carolina) such as INTRAWITE® CF, etc.; a Leucophor (available from Sandoz Chemicals Corp., Charlotte, North Carolina) such

35 as Leucophor BS, Leucophor BSB, Leucophor EKB, Leucophor

PAB, etc.; a Phorwite (available from Mobay Chemicals) such as Phorwite AR, Phorwite BBU, Phorwite BKL, Phorwite CL, Phorwite RKK, etc. and the like. Blancophor BBH, Calcofluor White M2R and Phorwite AR are the most preferred stilbene compounds.

Glidants are used in the process of this invention to keep the dried, coated pesticidal matrix particles from sticking together. In addition, the glidant may also provide some protection from ultraviolet radiation. Glidants suitable for use in this invention include talc, magnesium stearate, calcium stearate, calcium sulfate and the like or mixtures thereof, with talc being preferred.

Other compatible additives such as preservatives, stabilizers (trehalose), anti-foam agents, anti-mold agents, anti-fungal agents, anti-bacterial agents and the like may also be included in the matrices of the present invention. Clearly, anti-fungal agents and anti-bacterial agents generally would not be used when fungal pathogens and bacterial pathogens, respectively, are used.

The present invention also provides wettable powder pesticidal compositions which comprise about 0.5 to 40% by weight of a dispersing agent; about 1 to 10% by weight of a flow enhancing agent; about 10 to 70% by weight of a bulking agent; 0 to about 25% by weight of a wetting agent; 0 to about 35% by weight of a pH-modifying agent; and about 5 to 75% by weight of a coated pesticidal matrix prepared by the process of this invention.

Preferred wettable powder pesticidal compositions of the present invention are those comprising about 2 to 15% by weight of a dispersing agent; about 1 to 10% by weight of a flow enhancing agent; about 10 to 60% by weight of a bulking agent; 0 to about 15% by weight of a wetting agent; 0 to about 20% by weight of a pH-modifying agent;

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and about 5 to 75% by weight of a coated pesticidal matrix prepared by the process of this invention.

When the pesticidal agent is a biological agent, the wettable powder compositions of this invention preferably
5 comprise about 2 to 10% by weight of a dispersing agent; about 1 to 10% by weight of a flow enhancing agent; about 20 to 50% by weight of a bulking agent; about 2 to 20% by weight of a pH-modifying agent; and about 15 to 60% by weight of a coated biological agent matrix prepared by
10 the process of this invention.

Dispersing agents useful in the wettable powder pesticidal compositions of this invention include any of the conventional agents known in the art. Preferred dispersing agents are anionic agents, such as salts of
15 the condensation products of formaldehyde with the sulfonation products of polycyclic aromatic compounds, sodium lignosulfonate and the like or mixtures thereof with the sodium sulfonate of naphthalene formaldehyde condensates such as MORWET® D425 (available from Witco),
20 LOMAR® PW (available from Henkel, Ambler, Pennsylvania) and DARVAN® 1 (available from R.T. Vanderbilt Co., Norwalk, Connecticut) being most preferred.

Flow enhancing agents useful in the wettable powder pesticidal compositions of this invention include
25 conventional flow enhancing agents known in the art with silicates such as calcium silicates being preferred. MICRO-CEL® E (a synthetic calcium silicate hydrate available from Celite Corp., Lompoc, California) is the most preferred flow enhancing agent.

30 Bulking agents suitable for use in the compositions of the present invention include natural and synthetic clays and silicates, e.g., natural silicas such as diatomaceous earths; magnesium silicates such as talcs; magnesium aluminum silicates such as attapulgites
35 and vermiculites; aluminum silicates such as kaolinites,

5 with kaolin clay being the most preferred bulking agent.

10 polyethoxy ethanol, nonylphenoxy polyethoxy ethanol,
sodium dioctyl sulfosuccinate, sodium dodecyl benzene
sulfonate, sodium lauryl sulfate, sodium alkyl
naphthalene sulfonate, sodium sulfonated alkyl
carboxylate and the like or mixtures thereof. A mixture
15 of sodium alkyl naphthalene sulfonate and sodium
sulfonated alkyl carboxylate (MORWET® EFW available from
Witco, Houston, Texas) is a highly preferred wetting
agent.

glutaric acid, isophthalic acid, succinic acid, fumaric acid, adipic acid, and the like, and mixtures thereof. Citric acid is especially useful as the pH-modifying agent in the compositions of this invention. In the compositions of this invention, it is preferable to use a granular organic acid having a mean particle size greater than about 50 μm , preferably greater than about 100 μm . The use of a granular organic acid improves the storage stability of the wettable powder compositions of this

EXAMPLE 1

Preparation of coated pesticidal matrices using an ethyl acrylate/methacrylic acid copolymer

5 A mixture of V8vEGTDEL polyhedral inclusion bodies (PIBs) (12.43 g of technical material, 7.5 g of PIBs, about 1.27×10^{11} PIBs/gram, mean PIB size about $2.5 \mu\text{m}$), water (65.02 g), Blancophor BBH (28.04 g, mean particle size about $1 \mu\text{m}$), PEG 5000 (poly(ethylene glycol) average MW 5000, 14.0 g of a 10 wt/wt% solution), and Kollicoat[®] MAE 30 D (46.71 g) is stirred to obtain a slurry. The slurry is filtered through an 80 mesh screen and spray dried using a Büchi spray drier (model 190) to obtain the coated pesticidal matrix identified as composition 1 in Table II.

15 Using essentially the same procedure, but using the ingredients listed in Table I, the coated pesticidal matrices identified as compositions 2-17 in Table II are prepared.

TABLE I

- Pesticidal Agent
- a. V8vEGTDEL polyhedral inclusion bodies
 - 5 b. V8vEGTDEL-AaIT polyhedral inclusion bodies
 - c. Hydramethylnon
 - d. *Bacillus thuringiensis*
-
- 10 Ethyl Acrylate/Methacrylic Acid Copolymer
- e. Kollicoat[®] MAE 30 D
 - f. Eudragit[®] L 30 D
-
- 15 Plasticizer
- g. PEG 5000
 - h. PEG 8000
-
- 20 Stilbene Compound
- i. Blancophor BBH
 - j. Calcofluor M2R
-
- 25 UV-Protector
- k. Titanium dioxide
 - l. Charcoal
-
- 30 Additional Compound
- m. Antifoam A[®] (a polydimethylsiloxane and silica antifoam agent available from Dow Corning, Midland, Michigan)

TABLE II**Pesticidal Matrices**

<u>Composition</u>	<u>Pesticidal Agent</u>	<u>Ingredient / wt/wt%</u>				<u>Additional Compound</u>
		<u>Copolymer</u>	<u>Plasticizer</u>	<u>Stilbene Compound</u>	<u>UV - Protector</u>	
1	a/11.25	e/28.62	g/2.86	i/57.27	-	-
2	a/12.23	f/23.30	g/2.33	i/62.14	-	-
3	a/12.25	f/18.37	-	i/69.39	-	-
4	a/16.19	f/20.96	h/1.19	i/61.65	-	-
5	a/20.38	f/26.38	h/1.50	-	k/51.73	-
6	a/33.31	f/43.11	h/2.45	j/21.13	-	-
7	a/16.00	f/20.71	h/2.36	i/60.93	-	-
8	a/13.30	f/17.22	h/1.96	i/25.32	k/42.20	-
9	a/20.55	f/25.74	h/1.49	-	k/52.22	-

¹ Compositions may contain a small amount of residual water.

TABLE II (cont.)

<u>Composition</u>	<u>Pesticidal Agent</u>	<u>Ingredient / wt/wt%¹</u>				<u>Additional Compound</u>
		<u>Copolymer</u>	<u>Plasticizer</u>	<u>Stilbene Compound</u>	<u>UV - Protector</u>	
10	a/16.11	f/20.44	g/2.05	i/61.40	-	-
11	a/12.22	f/23.29	g/2.33	i/62.16	-	-
12	a/13.90	f/26.52	g/2.62	i/49.93	l/7.02	-
13	a/21.28	f/19.17	g/1.92	i/57.64	-	-
14	b/14.16	f/27.05	g/2.13	i/56.66	-	-
15	b/15.06	e/22.77	g/2.23	i/59.94	-	-
16	c/13.95	f/27.91	g/2.33	i/55.81	-	-
17	d/14.15	f/27.02	g/2.06	i/56.61	-	m/0.16

EXAMPLE 2

Preparation of coated pesticidal matrices using a
methyl methacrylate/methacrylic acid copolymer

A slurry is prepared by sequentially mixing
5 V8vEGTDEL polyhedral inclusion bodies (13.0 g of
technical material, 6.0 g of PIBs, about 1.27×10^{11}
PIBs/gram, mean PIB size about 2.5 μm), water, 56.6 g of
a copolymer slurry (previously prepared by mixing
Eudragit[®] S100 (30.0 g), water (166 g), 1 N ammonium
10 hydroxide solution (15.24 g) and triethyl citrate (15.0
g)), Blancophor BBH (14.0 g), talc (3.21 g), charcoal
(9.0 g), a solution of Calcofluor M2R (14.0 g) in water,
and water. The resultant slurry is then filtered through
an 80 mesh screen and spray dried using a Büchi spray
15 drier (model 190) to obtain the coated pesticidal matrix
identified as composition 18 in Table IV.

Using essentially the same procedure, but using the
ingredients listed in Table III, the coated pesticidal
matrices identified as compositions 19-26 in Table IV are
20 prepared.

TABLE III

Pesticidal Agent

- 5 a. V8vEGTDEL polyhedral inclusion bodies
b. V8vEGTDEL-AaIT polyhedral inclusion bodies
c. Yeast

Methyl Methacrylate/Methacrylic Acid Copolymer

- 10 d. Eudragit® S100
e. Eudragit® L100

Plasticizer

- 15 f. Triethyl citrate

UV-Protector

- 20 g. Charcoal

Stilbene Compound

- 25 h. Blancophor BBH
i. Calcofluor M2R

Glidant

- j. Talc
30

Additional Compound

- k. Citric acid
l. Microat® afa Complex (an antioxidant available from
Nurture Inc., Missoula, Montana)

TABLE IV

Pesticidal Matrices

<u>Composition</u>	<u>Pesticidal Agent</u>	<u>Ingredient / wt/wt%¹</u>					<u>Glidant</u>	<u>Additional Compound</u>
		<u>Copolymer</u>	<u>Plasticizer</u>	<u>UV-Protector</u>	<u>Stilbene Compound</u>			
18	a/11.89	d/14.86	f/7.43	g/17.84	h/27.75 i/13.87	j/6.36	-	
19	a/11.89	d/14.86	f/7.43	g/17.84	h/35.08 i/ 6.54	j/6.36	-	
20	a/12.36	e/15.45	f/7.72	g/18.54	h/37.08	j/7.72	k/1.13	
21	a/12.12	e/15.15	f/7.58	g/18.18	h/36.36	j/7.58	k/1.01 l/2.02	
22	b/10.90	d/16.59	f/8.30	g/16.59	h/38.06 i/4.36	j/5.20	-	
23	b/8.68	d/17.59	f/8.81	g/16.77	h/38.47 i/4.41	j/5.26	-	
24	b/8.77	d/16.94	f/8.47	g/17.20	h/38.86 i/4.45	j/5.31	-	
25	a/10.90	d/16.59	f/8.30	g/16.59	h/38.06 i/4.36	j/5.20	-	
26	c/21.61	e/40.36	-	-	h/38.04	-	-	

¹ Compositions may contain a small amount of residual water.

EXAMPLE 3

**Preparation of coated pesticidal matrices using
a methacrylic acid/methyl acrylate/methyl methacrylate
copolymer**

5 A mixture of chlorfenapyr (3.00 g, mean particle
size about 2.5 μ m), water (100.00 g), Blancophor BBH
(12.00 g, mean particle size about 1 μ m), triethyl
citrate (0.23 g), a 20% solution of Preparation 4110D
(22.50 g), talc (3.00 g), and MORWET®D425 (1.50g) is
10 stirred to obtain a slurry. The slurry is filtered
through an 80 mesh screen and spray dried using a Büchi
spray drier (model 190) to obtain the coated pesticidal
matrix identified as composition 27 in Table VI.

15 Using essentially the same procedure, but using the
ingredients listed in Table V, the coated pesticidal
matrices identified as compositions 28-32 in Table VI are
prepared.

TABLE V

Pesticidal Agent

- 5 a. Chlorfenapyr
b. Hydramethylnon
c. 1-(6-Chloro-3-pyridyl)-2-(nitromethylene)imidazolidine
d. V8vEGTDEL-AaIT polyhedral inclusion bodies

10 Methacrylic Acid/Methyl Acrylate/Methyl Methacrylate
Copolymer

Preparation 4110D

Plasticizer

- 15 Triethyl citrate

Stilbene Compound

- e. Blancophor BBH
f. Calcofluor M2R

20

UV-Protector

Charcoal

Glidant

- 25 Talc

Additional Compound

MORWET®D425

TABLE VI
Pesticidal Matrices

<u>Composition</u>	<u>Pesticidal Agent</u>	<u>Preparation 4110D</u>	<u>Ingredient / wt/wt%¹</u>				
			<u>Triethyl Citrate</u>	<u>Stilbene Compound</u>	<u>Charcoal</u>	<u>Talc</u>	<u>MORWET® D425</u>
27	a/12.38	18.57	0.95	e/49.53	-	12.38	6.19
28	a/9.01	18.02	0.90	e/36.04 f/9.01	13.51	9.01	4.50
29	b/12.38	18.57	0.95	e/49.53	-	12.38	6.19
30	b/9.01	18.02	0.90	e/36.04 f/9.01	13.51	9.01	4.50
31	c/13.97	21.12	1.05	e/42.76	-	13.97	7.13
32	d/9.36	18.71	1.87	e/37.42 f/4.57	18.71	9.36	-

¹Compositions may contain a small amount of residual water.

EXAMPLE 4

Preparation of a coated pesticidal matrix using a methyl methacrylate/methacrylic acid copolymer, REAX[®] 85A and Indulin[®] C

5 A mixture of V8vEGTDEL polyhedral inclusion bodies
(13.0 g of technical material, 6.0 g of PIBs, about 1.27×10^{11} PIBs/gram, mean PIB size about 2.5 μm) and ammonium
hydroxide solution (15.0 g, pH 9.5) is stirred for 15
minutes, treated with REAX[®] 85A (0.18 g, a sodium
10 lignosulfonate available from Westvaco, Charleston
Heights, South Carolina), stirred for 15 minutes, treated
with Indulin[®] C (12.0 g of a 2% solution, pH 11, a sodium
lignate available from Westvaco), stirred for one hour,
and adjusted slowly to pH 4.5 with dilute sulfuric acid
15 over 2.5 hours. After stirring for 45 minutes, the
polyhedral inclusion body mixture is mixed with the
copolymer slurry described in Example 2 (56.6 g),
Blancophor BBH (14.70 g), talc (3.21 g), charcoal (9.0
g), a solution of Calcofluor M2R (3.30 g) in water, and
20 water to obtain a slurry. The slurry is filtered through
an 80 mesh screen and spray dried using a Büchi spray
drier (model 190) to obtain the coated pesticidal matrix
identified as composition 33 in Table VII.

TABLE VII

Composition 33

<u>Ingredient</u>	<u>wt/wt%</u>
V8vEGTDEL polyhedral inclusion bodies	12.53
Eudragit® S100	15.66
Triethyl citrate	7.83
Charcoal	18.80
Blancophor BBH	30.70
Calcofluor M2R	6.89
Talc	6.70
Indulin® C	0.50
REAX® 85A	0.38

5

EXAMPLE 5

Preparation of wettable powder pesticidal compositions

10 The coated pesticidal matrix identified as composition 18 in Table IV (23.13 g) is added to a premix of MORWET® EFW (3.84 g), MORWET® D425 (7.68 g), kaolin clay (23.03 g), MICRO-CEL® E (2.30 g), and citric acid (11.52 g). The resultant mixture is blended to obtain the wettable powder composition identified as composition 15 34 in Table VIII.

Using essentially the same procedure, the wettable powder compositions identified as compositions 35-53 in Table VIII are prepared.

TABLE VIII
Wettable Powder Pesticidal Compositions
Ingredient / wt/wt%

Composition	Coated Pesticidal					
	Matrix ¹	MORWET® EFW	MORWET® D425	Kaolin Clay	MICRO-CEL®E	Citric Acid
34	18/32.35	5.37	10.74	32.21	3.22	16.11 ²
35	1/30.77	5.50	10.99	32.97	3.30	16.48 ²
36	2/25.91	5.88	11.76	35.29	3.53	17.63 ²
37	9/16.05	6.67	13.32	39.98	4.00	19.99 ²
38	11/25.91	5.88	11.76	35.28	3.53	17.64 ²
39	12/16.98	7.56	15.11	49.81	4.98	5.56 ²
40	13/19.80	6.37	12.73	38.20	3.82	19.09 ²
41	15/21.52	7.13	14.30	47.10	4.70	5.25 ²
42	19/32.35	5.37	10.74	32.21	3.22	16.11 ²
43	20/31.12	5.47	10.94	32.79	3.28	16.40 ²
44	21/31.73	5.42	10.84	32.50	3.25	16.25 ²

¹ The coated pesticidal matrix is identified by the composition number from Tables II, IV or VI.

² Mean particle size about 1-3 μm .

³ Mean particle size greater than about 100 μm .

Ingredient / wt/wt%

¹ The coated pesticidal matrix is identified by the composition number from Tables II, IV or VI.

² Mean particle size about 1-3 μm .

³ Mean particle size greater than about 100 μm .

EXAMPLE 6

Evaluation of wettable powder pesticidal compositions of this invention and a wettable powder pesticidal composition disclosed in EP 697170-A1 against tobacco budworms

Wettable powder compositions 34, 36, 37 and 43, and a control composition, identified below, are tested for efficacy against neonate tobacco budworms, *H. virescens*, on cotton variety IAC-22 through bioassay of field-treated foliage. Each composition is mixed with water, 0.2 w/v% KINETIC® (nonionic surfactant mixture available from Helena Chemical Co., Memphis, Tennessee), and 3.5 w/v% MIRASPERSE® (2-hydroxypropyl ether starch available from A.E. Staley Manufacturing Co., Decatur, Illinois). In addition, 0.1 w/v% citric acid is added to the aqueous control composition. Treatments are applied with a CO₂ backpack sprayer calibrated to deliver 200 L/ha using 2 ft boom with hollow-cone nozzles (3/row; 1 centered and 2 drop).

For bioassay, leaves are collected 1-2 hours following application for initial activity and 1, 2, 3, and 4 days after treatment for residual activity. The treated leaves are placed in petri dishes with moist filter papers (1 leaf/dish; 4 larvae/dish; 16 dishes/-treatment with a total of 64 larvae/treatment/sampling period). After allowing the larvae to feed on the treated leaves for four days, they are transferred to diet trays containing pieces of untreated cotton leaves; one larva/cell. After 4 days, the surviving larvae are counted. The results are summarized in Table IX.

As can be seen from the data in Table IX, compositions containing coated pesticidal matrices prepared by the process of the present invention, in general, have greater residual activity against

H. virescens than the control composition prepared by the aqueous process described in EP 697170-A1. In particular, composition 34 has significantly greater residual activity than the control composition. This is an especially surprising discovery because the copolymer used in composition 34 and the control composition is the same Eudragit® S100.

Control Composition	
<u>Ingredient</u>	<u>wt/wt%</u>
¹ Coated pesticidal agent	25.14
MORWET® EFW	5.94
MORWET® D425	11.89
Kaolin Clay	35.64
MICRO-CEL® E	3.56
Citric Acid	17.83

¹Prepared according to the aqueous process described in EP 697170-A1. The coated pesticidal agent contains 15.31 wt/wt% V8vEGTDEL polyhedral inclusion bodies, 15.31 wt/wt% Eudragit® S100, 0.43 wt/wt% PEG 8000, 23.04 wt/wt% charcoal and 45.92 wt/wt% Blancophor BBH.

TABLE IX
Percent Mortality of *H. virescens*
on Cotton variety IAC-22

<u>Treatment</u>	<u>Days After Treatment</u>				
	<u>0</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Composition 34	100	92	95	89	75
Composition 36	98	97	77	75	66
Composition 37	97	94	92	77	67
Composition 43	98	95	95	86	80
Control composition	95	86	83	73	69
Untreated	5	2	5	8	6

EXAMPLE 7

Evaluation of wettable powder pesticidal compositions against tobacco budworms on cotton and lettuce

5 Compositions 39 and 49 from Table VIII are tested for efficacy against neonate tobacco budworms, *Heliothis virescens*, on lettuce variety Green-Towers and cotton variety Delta-Pine 51 through bioassay of field-treated foliage. The plots are strips of cotton and lettuce (ca. 10 40 ft long) with 3 ft row spacing. Each composition is mixed with water and applied at 8×10^{11} polyhedral inclusion bodies/acre. DIPEL® 2X (*Bacillus thuringiensis* var. Kurstaki, available from Abbott Laboratories, North Chicago, Illinois) is applied at 1.0 lb product/acre as a standard. 15 Treatments are applied with a CO₂ backpack sprayer calibrated to deliver 20 gallons per acre using a 2 ft boom with hollow-cone nozzles (3/row; 1 centered and 2 drop).

For bioassay, leaves are collected 1-2 hours 20 following application for initial activity and 2, 3, 4 and 5 days after treatment for residual activity. The treated leaves are placed in petri dishes with moist filter papers (1 leaf/dish; 4 larvae/dish; 16 dishes/-treatment with a total of 64 larvae/treatment/sampling 25 period). After allowing the larvae to feed on the treated leaves for two days, they are transferred to diet trays; one larva/cell. The surviving larvae are also counted at 2, 4, 6 and 8 days after transfer to diet. The results are summarized in Tables X and XI.

30 As can be seen from the data in Tables X and XI, the pesticidal compositions of this invention (compositions 39 and 49) have greater residual activity against tobacco budworms after 4, 6 and 8 days on diet than DIPEL® 2X.

TABLE X
Percent Mortality of Tobacco Budworms on Cotton

<u>Treatment</u>	<u>Days After Transfer to Diet</u>	<u>Days After Treatment</u>				
		<u>0</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Composition 39	0	4	3	2	1	2
	2	24	9	6	3	4
	4	49	23	14	6	13
	6	50	27	16	7	15
	8	51	27	16	8	15
Composition 49	0	2	3	2	0	5
	2	52	17	9	7	6
	4	90	57	29	11	14
	6	91	59	31	15	16
	8	91	59	33	16	16
DIPEL® 2X	0	29	9	6	2	4
	2	37	13	7	4	6
	4	56	14	10	4	6
	6	56	14	12	5	6
	8	56	14	12	5	6
Untreated	0	1	2	1	1	2
	2	1	4	2	3	4
	4	2	6	3	3	5
	6	2	6	4	3	5
	8	2	6	4	3	5

TABLE XI
Percent Mortality of Tobacco Budworms on Lettuce

<u>Treatment</u>	Days After Transfer to Diet	<u>Days After Treatment</u>				
		<u>0</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Composition 39	0	27	5	2	5	1
	2	72	36	16	20	11
	4	94	84	62	55	50
	6	95	85	67	59	52
	8	95	86	67	60	52
Composition 49	0	16	3	7	1	6
	2	73	24	23	18	16
	4	98	88	78	62	55
	6	99	88	85	62	58
	8	99	88	85	62	59
DIPEL® 2X	0	100	53	42	45	29
	2	100	70	50	57	35
	4	100	70	56	58	37
	6	100	70	56	58	38
	8	100	70	56	58	38
Untreated	0	2	1	2	2	4
	2	2	2	5	2	6
	4	4	5	6	3	9
	6	4	5	6	4	10
	8	4	5	6	6	10

EXAMPLE 8

Evaluation of non-irradiated and irradiated wettable
powder compositions against *Heliothis virescens*

Plastic bioassay trays containing 32 open-faced
5 wells (4 x 4 x 2.5 cm, L x W x H) per tray are utilized
as test arenas in this evaluation. Five mL of Stoneville
diet (soybean/wheat germ) is poured into each well and
allowed to harden. Aqueous suspensions of the wettable
powder pesticidal compositions are evenly spread over the
10 surface of the hardened diet to provide 2×10^3 V8vEGTDEL
polyhedral inclusion bodies per well. Half of the trays
are placed under ultraviolet lamps (two FS40UVB bulbs set
30 cm above the trays, Atlantic Ultraviolet Corp., Bay
Shore, NY) for four hours. All trays are then infested
15 with one three-day-old *H. virescens* larva per well. The
wells are covered with a vented, clear plastic sheet and
held under constant fluorescent light at a temperature of
about 27 °C. After ten days, the wells are examined and
larval mortality measurements are made. The results are
20 summarized in Table XII.

Advantageously, the wettable powder pesticidal
compositions of this invention (composition numbers 35,
36, 38 and 40) retain at least 73 percent of their
original activity after being exposed to ultraviolet
25 light for 4 hours.

TABLE XII

Evaluation Of Non-Irradiated and Irradiated Wettable
Powder Pesticidal Compositions Against *H. Virescens*

<u>Wettable Powder Composition</u> ¹	<u>Irradiation Exposure (hours)</u>	<u>Percent Larval Mortality</u>
35	0	98
	4	74
36	0	98
	4	80
38	0	97
	4	75
40	0	97
	4	71

5 ¹ Composition number from Table VIII.

EXAMPLE 9

Field evaluation of wettable powder pesticidal compositions against tobacco budworms on tobacco in North Carolina

- 5 A field evaluation is conducted on tobacco grown near Clayton, North Carolina. A wettable powder composition of this invention (composition 46) at 2×10^{11} , 5×10^{11} , and 8×10^{11} bodies/acre, *Bacillus thuringiensis* (DIPEL[®] 2X, Abbott Laboratories) at 1.0 lb
- 10 wettable powder (WP)/acre, and acephate (ORTHENE[®] 75SP, available from Valent USA, Walnut Creek, California) at 0.75 lb active ingredient (ai)/acre are compared for efficacy against *H. virescens*. Biological materials are suspended in water containing an insect gustatory
- 15 stimulant (PHEAST[®] available from AGRISENSE, Fresno, California); aqueous dilutions of acephate contained no PHEAST[®]. Treatments and untreated check are replicated four times (small plots) in a randomized complete block design. By using fine-hair brushes, 1- to 2-day old
- 20 laboratory-reared *H. virescens* are placed on the underside of leaves in each plot. Natural infestation of *H. virescens* also occurred at the test site. Treatments are applied to tobacco about 2 hours before each artificial larval infestation on days 1 and 8.
- 25 Treatments are applied with a tractor-mounted, CO₂-pressurized boom sprayer which is calibrated to deliver 25 gallons/acre through a single D2-33 nozzle centered over each tobacco row. Boom pressure during application is 60 lb/in².
- 30 At 2 and 5 days after first application and 5 and 9 days after second application, live *H. virescens* are counted on 20 plants in each plot. Additionally, visual estimate of leaf damage caused by larval feeding is made

14 days after the second application using the rating scale shown below. The results are summarized in Table XIII.

Rating Scale

<u>Rating</u>	<u>Meaning</u>
4	Severe Damage
3	Heavy Damage
2	Moderate Damage
1	Slight Damage
0	No Damage

5

As can be seen from the data in Table XIII, the wettable powder composition of this invention (composition 46) provides good control of *H. virescens* on tobacco. In fact, on day 17 of the test, the invention composition provides greater control of *H. virescens* than DIPEL® 2X and acephate.

10

TABLE XIII**Field Evaluation of Wettable Powder Compositions - North Carolina**

<u>Treatment</u>	<u>Rate</u>	<u>Mean Number of</u> <u>Live Larvae per 20 Plants</u>				<u>Mean Plant</u> <u>Injury on Day</u> <u>22 of Test</u>
		<u>Day of Test</u>				
		<u>3</u>	<u>8</u>	<u>13</u>	<u>17</u>	
Composition 46	2 x 10 ¹¹ bodies/acre	7.8	6.2	1.8	0.5	0.4
	5 x 10 ¹¹ bodies/acre	6.8	6.2	1.2	0.2	0.3
	8 x 10 ¹¹ bodies/acre	7.0	6.0	1.0	0.5	0.3
DIPEL® 2X	1.0 lb of WP/acre	5.5	5.0	1.2	2.5	0.1
Acephate	0.75 lb of ai/acre	6.0	5.8	1.2	0.8	0.2
Untreated		11.2	8.2	8.8	9.0	1.8

EXAMPLE 10

Field evaluation of wettable powder pesticidal compositions against tobacco budworms on tobacco in Georgia

5 A field evaluation is conducted on flue-cured tobacco (var. K-236) grown near Tifton, Georgia. A wettable powder composition of this invention (composition 47) at 2×10^{11} , 5×10^{11} , and 8×10^{11} bodies/acre, *Bacillus thuringiensis* (DIPEL® 4L, available from Abbott Laboratories) at 1.0 pint/acre, and methomyl (LANNATE® 2.4L, available from DuPont, Wilmington, Delaware) at 0.6 lb active ingredient (ai)/acre are compared for efficacy against *H. virescens*. Biological materials are suspended in water containing an insect gustatory stimulant (COAX® available from CCT Corp., Carlsbad, California) at 2.0 pints/acre; aqueous dilutions of methomyl contained no COAX®. Treatments and untreated check are replicated four times in a randomized complete block design. A treatment replicate consists of a five-row by 20 ft plot of tobacco. Treatments are applied to tobacco on days 1, 5, 9, 17 and 22 of the test. Treatments are applied with a backpack, CO₂-pressurized boom sprayer which is calibrated to deliver 20.7 gallons/acre through three TX12 (Spraying Systems, Wheaton, IL) hollow-cone nozzles per row (one nozzle above center of the row and one nozzle directed at each of the two sides of the row). Boom pressure during application is 40 lb/in².

On days 5, 8, 12, 22, 26 and 29 of the test, live *H. virescens* are counted on 20 plants in each plot. The results are summarized in Table XIV.

As can be seen from the data in Table XIV, the wettable powder composition of this invention (composition 47) provides good control of *H. virescens*.

EXAMPLE 11

Evaluation of UV stability of wettable powder compositions comprising chlorfenapyr

Wettable powder compositions 50 and 51 from Table VIII, and a control composition identified below are evaluated for UV stability. An aqueous suspension of each test composition is applied to plastic petri dishes (100 mm x 15 mm) using a belt sprayer with nozzles calibrated to provide 400 l/ha. The test materials are applied at rates to provide the equivalent of 0.5, 1.0 and 5.0 g of chlorfenapyr per hectare. The dishes are dried and exposed to UV light using either a UV-B lamp (280-315 nm) or natural light for various periods of time. Three second-instar tobacco budworm larvae (*Heliothis virescens*) are then placed in each dish and the dishes are covered. After holding the dishes at 26.7°C for 48 hours, the surviving larvae are counted. The results are summarized in Tables XV and XVI.

As can be seen from the data in Tables XV and XVI, chlorfenapyr treatments made with the wettable powder compositions of this invention are significantly more stable to UV exposure than the control composition which does not incorporate chlorfenapyr into a pesticidal matrix.

Control Composition

<u>Ingredient</u>	<u>wt/wt%</u>
Chlorfenapyr (tech.)	5.43
MORWET®EFW	8.60
MORWET®D425	17.21
Kaolin Clay	56.75
MIRO-CEL®E	5.67
Citric Acid ¹	6.34
¹ Mean particle size about 1-3 μ m	

5

TABLE XV

Evaluation of UV (natural light) Irradiated
Chlorfenapyr Wettable Powder Compositions

<u>Wettable Powder Composition</u>	<u>Irradiation Exposure (days)</u>	<u>Percent Larval Mortality</u>	
		<u>1.0 g/ha</u>	<u>0.5 g/ha</u>
50	0	100	86
	2	74	58
	3	28	34
51	0	100	91
	2	100	75
	3	63	48
Control Composition	0	100	97
	2	54	34
	3	15	22

TABLE XVI
Evaluation of UV-B Lamp Irradiated Chlorfenapyr
Wettable Powder Compositions

Wettable Powder Composition	Irradiation Exposure (hours)	Percent Larval Mortality	
		5.0 g/ha	1.0 g/ha
50	0	100	100
	8	100	76
	22	100	76
	37	100	0
51	0	100	100
	8	100	47
	22	100	21
	37	56	0
Control Composition	0	100	100
	8	100	31
	22	100	24
	37	14	6